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→ Formation of Aluminon nitrides, organometallic compounds

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PREPARATION OF SiC/AlN SOLID SOLUTIONS

USING ORGANOMETALLIC PRECURSORS

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SUMMARY

The co-pyrolysis of organoaluminum and organosilicon compounds was investigated as a potential source of SiC/AlN solid solutions. Using two different co-pyrolysis methods, homogeneous mixtures of organoaluminum amides and both a vinylic polysilane and a polycarbosilane were converted to a preceramic solid that transformed to crystalline SiC/AlN solid solutions at <1600 °C. Moreover, the liquid, polymeric, form of these precursor mixtures provides a potential processing advantage that may be useful for ceramic matrix preparation and other applications. In the course of this work new precursors to both AlN and SiC were identified and their structures and pyrolysis reactions were investigated, providing useful information regarding structure/pyrolysis chemistry relationships for such precursor systems.

In addition, modifications of this co-pyrolysis approach to SiC/AlN solid solutions were employed to obtain mixed-phase SiC/AlN, silicon nitride, silicon nitride/AlN and β' -SiAlON ceramics. The composition, phase distribution, and microstructure of these ceramics were examined by elemental analysis, x-ray powder diffraction, SEM/TEM, and other methods. This effort was successful not only in yielding processible precursors to the desired SiC/AlN solid solutions, but also in providing a general route to a wide range of other compositions and phases in the Si-C-Al-O-N system.

INTRODUCTION

The chief objective of this work has been to develop processible precursors to SiC/AlN solid solutions that could be used to obtain this material at convenient temperatures and pressures in the desired final form for structural and electronic ceramic applications. Such solid solutions are of interest both as electronic materials (variable band gap semiconductors, electronic substrates, etc.) and structural materials (ceramic fibers and matrices for high temperature structural composites). It has previously been shown that, unlike SiC alone, such solid solutions resist crystallographic transformation with temperature cycling and exhibit a single 2H (wurzite) structure over a wide range of temperatures and compositions. Moreover, this previous work has suggested that grain growth of SiC is inhibited by small additions of AlN, which may allow preparation of ceramic fiber with better strength retention at high temperatures. These solid solutions have been previously obtained in homogeneous form only at very high temperatures (>2300 C) in a hot-press and are quite difficult to obtain in useful final forms (fibers, matrices, monoliths or films) by conventional ceramic processing methods due to the intrinsically low solid state diffusivities of the component materials¹.

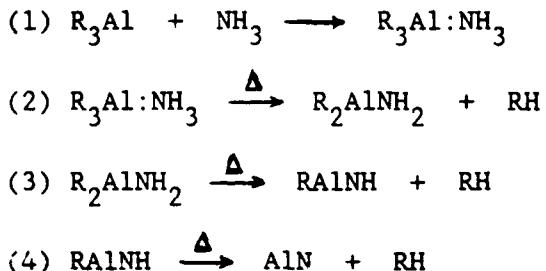
The approach chosen to meet this objective involved the co-pyrolysis of molecularly mixed precursors to SiC and AlN. This approach has necessitated the identification and, in some cases, the development of appropriate miscible, liquid, organometallic precursors to the two components. These precursors were required either to react with one another on heating to fix the relative positions of Si and Al in the solid or to undergo pyrolysis at comparable temperatures and rates to enable retention of the homogeneous atomic distribution in the original solution.

As described below, this approach has been successful not only in yielding the desired SiC/AlN solid solutions at temperatures well below that previously required to obtain these phases, but also in providing a general route to a wide range of other compositions and phases in the Si-C-Al-O-N system. In addition to these co-pyrolysis studies, synthesis work on both AlN and SiC precursors has led to promising new compounds, polymers, and approaches to these important classes of ceramic materials.

This research program has also enabled the development of a state-of-the-art laboratory for ceramic precursor synthesis and study at RPI, with appropriate equipment and facilities for a wide range of synthesis and property evaluation studies. The current effort on ceramic precursors involves three postdoctoral associates and ten graduate and undergraduate students in chemistry and materials engineering with support from four different sources.

Our collaboration with Dr. Glen Slack at General Electric CRD as well as several other members of the GE research and support staff under a subcontract to GE CRD aided considerably in the pursuit of this research program. This has provided access to valuable materials fabrication and characterization facilities as well as expert advice which has aided in the interpretation of the results of these measurements. We have also maintained contact with, and have obtained valuable insights from discussions with, the staff of the AFWAL/MLLM lab at Wright-Patterson AFB through periodic visits and report distributions.

The starting point for this research effort was the prior work by the P.I. at GE CRD on AlN synthesis. Using the following series of reactions, high purity AlN powders were prepared in high yield and thin AlN films were deposited on Si and other substrates by chemical vapor deposition^{2,3}.



where R = alkyl

In addition, much useful information was obtained about the structure, properties, and thermolysis reactions of the various intermediates involved in the above reaction sequence. This information has been invaluable in the subsequent application of this chemistry, under our AFOSR contract, to the preparation of SiC/AlN ceramics.

In particular, the organoaluminum amide intermediates, R_2AlNH_2 , were found to be cyclic, 6-membered ring compounds of the type, $[R_2AlNH_2]_3$, which exhibit solubility in hydrocarbon solvents and, in the case of R = CH_3 , sufficient volatility for use in CVD of AlN. Moreover, the temperatures at which these compounds undergo pyrolysis to the polymeric, insoluble RAlNH intermediates was found to depend on the nature of the R group, with a general increase in decomposition temperature as the size of the R group increases. The application of these precursors, along with both new and previously obtained SiC precursors to obtain the solid solutions and various other ceramic products are described in the next section of this report as well as in the attached reprints and preprints (Appendix I).

SUMMARY OF RESEARCH ACCOMPLISHMENTS

Co-Pyrolysis of $[(iso\text{-}butyl)}_2AlNH_2]_3$ with Organosilanes

On the basis of its higher decomposition temperature relative to the corresponding Me and Et compounds, the $[(iso\text{-}butyl)}_2AlNH_2]_3$ compound was employed as the AlN source in our initial co-pyrolysis experiments. This liquid compound was mixed with a polycarbosilane of the approximate composition, $[Si(CH_3)HCH_2]_n$, (vide infra) and co-pyrolyzed to obtain SiC/AlN ceramics. Initially, this pyrolysis was carried out by heating the miscible liquid mixture at ca. 170-200°C until the mixture had solidified sufficiently to obtain a waxy solid. This was then transferred to a furnace for further heating under nitrogen. The initial product after heating to 1000°C was poorly crystalline, but further heating to 1400-1600°C eventually resulted in an intimate mixture of crystalline β (3C)-SiC and 2H

AlN. This mixture was finally converted to a SiC/AlN solid solution by heating to 2000°C under 100 PSI Ar pressure. In contrast, substituting ammonia for nitrogen during the heating to 1000°C, led to a mixture of 2H AlN and Si_3N_4 , after annealing in nitrogen to 1400-1600°C. In this case, the proportion of α - to β - Si_3N_4 was found to depend on the amount of AlN precursor used, with the proportion of β - Si_3N_4 increasing with AlN addition (see paper 1 in Appendix I for further details).

A subsequent analysis of the TGA behavior of the component SiC and AlN precursors showed that these materials decomposed at substantially different temperatures, with the AlN precursor converting to the insoluble RAlNH intermediate well before the SiC precursor begins to decompose. The opalescence of the precursor mixture after heating to 170-200°C is suggestive of a suspension of the RAlNH in the partially converted polycarbosilane. It is interesting to note, however, that both TGA and bulk pyrolysis studies of mixtures of this low-yield polycarbosilane precursor and the $[(\text{iso-butyl})_2\text{AlNH}_2]_3$ show a substantial improvement in the overall ceramic yield (see below). This indicates that chemical interaction of the SiC and AlN precursors or their reaction products is occurring at some point in the pyrolysis.

The "Hot-Drop" Approach

The information obtained from the TGA and co-pyrolysis studies suggested that RAlNH phase separation from the liquid polycarbosilane might be avoided by carrying out the pyrolyses at elevated temperatures, where the rates of pyrolysis of both precursors were sufficiently high. Thus, mixtures of the liquid R_2AlNH_2 (R = iso-butyl or ethyl) and either the $[\text{Si}(\text{CH}_3)\text{HCH}_2]_n$ polycarbosilane or a polysilane of the approximate composition $[(\text{Me}_3\text{Si})_{0.5}(\text{CH}_2\text{CHSi}(\text{Me}))_{1.0}(\text{SiMe}_2)_{1.0}]_n$ obtained from C. Schilling of Union Carbide Corp.⁴ were dropped slowly from a syringe into a quartz reactor which was preheated to 500-650°C while a stream of ammonia was added. The initially obtained white powder was further heated under nitrogen or ammonia in a furnace to 1000°C and subsequently under nitrogen to 1400-1800°C, until sufficiently crystalline for XRD analysis. This approach, hitherto referred to as "the hot-drop approach", has led to a wide range of different Si-C-Al-(O)-N phases, depending on the details of the hot-drop procedure and the subsequent heating.

The composition and phase distribution of the ceramic product obtained in these hot drop reactions was found to depend intimately on such variables as the temperature of the quartz reactor, the use of ammonia or nitrogen at various stages of the pyrolysis, and the oxygen content and structure of the two precursors. Initial results indicate that virtually any desired phase in the Si-C-Al-O-N system can be obtained by proper control of these variables. For example, by maintaining the quartz reactor at 600°C or below and conducting the further heating under nitrogen, solid solutions of SiC/AlN were obtained on crystallization of the mixture at 1600°C. XRD data of the product indicates two peaks in the region between the 2H-SiC and 2H-AlN reference positions, which may correlate with two main solid solution phases, as was predicted by the phase diagram of Ruh and Zangvil¹. Subsequent TEM/SAD studies of this powder carried out at GE

CRD confirmed the presence of two distinct 2H SiC/AlN phases with Si/Al ratios consistent with expectations from the XRD peak positions.

Alternatively, heating the product from the hot-drop reaction of the organosilicon/dialkylaluminum amide mixture to 1000°C under ammonia was found to yield mixtures of Si_3N_4 and AlN, presumably due to ammonolysis of the Si-C bond at elevated temperature and resultant separation of the apparently immiscible Si_3N_4 and AlN phases. Further details of these studies can be found in the attached preprint and reprint (papers 2 and 3 in Appendix I). The range of products obtained from this "hot-drop" process was later extended further by the discovery that the product of certain "hot-drop" reactions carried out at 625°C under ammonia could be converted to β' -SiAlON on heating in nitrogen to 1490°C. Generally, β' -SiAlON's are prepared by reaction of β - Si_3N_4 and Al_2O_3 at temperatures greater than 1600°C⁵. The observation of the characteristic XRD pattern of a β' -SiAlON from our precursor system after heating to only 1490°C⁵ suggested that the "hot-drop" approach also has utility as a lower temperature route to these important ceramic materials. In the initial experiments the source of the oxygen incorporated in the ceramic β' -SiAlON product was not clearly identified; however, it is suspected that the quartz reactor used for these hot-drop reactions was serving as the oxygen source in cases where the reactor temperature was raised above 600°C. It was later found that the oxygen could be added in a more controlled manner by employing Et_2AlOEt as the Al-containing precursor in place of the organoaluminum amide in hot-drop reactions carried out in ammonia at around 500°C. In this way the proportion of Al to O could be held to the 1:1 ratio required for the β' -SiAlON phase and the nitrogen could be provided entirely from the ammonia atmosphere. A range of β' -SiAlON compositions have now been prepared by this approach and were characterized by both XRD and TEM. The expected expansion of the β - Si_3N_4 lattice dimensions on replacement of Si-N units by Al-O was observed in the XRD of these materials with a close correspondence between the composition observed by electron microprobe and that calculated from the lattice dimensions. Subsequent analysis by TEM/SAD confirmed the single-phase, β' -SiAlON identity of these products.

Co-Pyrolyses Involving $[(\text{ethyl})_2\text{AlNH}_2]_3$

In the last few months of this program, an alternative route to SiC/AlN solid solutions was discovered which obviates the need for the "hot-drop" approach and provides a system of much greater potential utility for ceramic processing. This method involves a relatively small change in the organoaluminum precursor employed in the co-pyrolysis reactions. Unexpectedly, it was found that replacement of the $[(\text{iso-butyl})_2\text{AlNH}_2]_3$ used previously by the corresponding ethyl derivative, $[(\text{ethyl})_2\text{AlNH}_2]_3$, in the co-pyrolysis with the polycarbosilane, $[\text{Si}(\text{CH}_3)\text{HCH}_2]_n$, resulted in the eventual production of a SiC/AlN solid solution on heating and subsequent annealing, without requiring the rapid increase in temperature involved in the "hot-drop" process. The detailed nature of the chemistry involved here and the reason for the difference in behaviour of the two organoaluminum precursors is not yet known for certain; however, based on preliminary nmr

studies, it appears that the ethyl compound undergoes reaction with the polycarbosilane at an early stage in the co-pyrolysis, thereby fixing the relative distribution of Al and Si atoms in the precursor mixture and preventing the separation of the insoluble organoaluminum imide from this mixture. The result, after completion of the pyrolysis in nitrogen to 1000°C, is an amorphous preceramic material which crystallizes directly to a SiC/AlN solid solution at ca. 1500°C. This simple modification in the dialkylaluminum amide structure now enables the direct use of such precursor mixtures in ceramic processing to obtain SiC/AlN solid solutions, as might be required, for example, in ceramic matrix preparation by liquid phase infiltration of fiber preforms.

Preparation and Study of New AlN and SiC Precursors

In addition to these studies of co-pyrolysis of organo-silicon and -aluminum compounds, several new precursors to both SiC and AlN have been prepared and studied during the period of the present contract. Studies of AlN precursors have included both further derivatives of the R_2AlNH_2 type, as well as alkylaluminum adducts of ethylenediamine and pyrimidine. Our work on AlN precursor synthesis has led to a novel $[(\text{t}\text{e}\text{r}\text{t}\text{-b}\text{u}\text{t}\text{y}\text{l})_2AlNH_2]_3$ derivative whose crystal structure solution reveals an unprecedented planar $(\text{AlN})_3$ ring, presumably resulting from 1,3 steric interactions between the large *tert*-butyl substituents. This work is summarized in two papers on the structure and properties of the R_2AlNH_2 precursors (papers 3 and 4 in Appendix I). Studies of the ethylenediamine and pyrimidine adducts with R_3Al ($R = \text{CH}_3, \text{C}_2\text{H}_5$) yielded both oligimeric and polymeric derivatives upon heating to eliminate RH. These compounds yield AlN on pyrolysis in ammonia. Along with the new R_2AlNH_2 compounds, they are promising candidates for the synthesis of Si-Al-C-(O)-N ceramics.

We have recently added another compound to the family of alkylaluminum:ammonia adducts. This compound, R_3AlNH_3 , with $R = \text{CH}_2\text{Si}(\text{CH}_3)_3$, is of particular interest in that it contains both Si and Al. It has not yet been fully characterized or studied; however, it provides an interesting counterpart to our *t*-butyl compound and the $R = \text{Si}(\text{CH}_3)_3$ derivative studied by Paine and co-workers⁷. The latter compound was reported to give an Al and Si containing ceramic on pyrolysis. The planned comparison of the pyrolysis chemistry of these two compounds as well as the structures of the three R_2AlNH_2 derivatives [$R = \text{t}\text{e}\text{r}\text{t}\text{-b}\text{u}\text{t}\text{y}\text{l}, \text{CH}_2\text{Si}(\text{CH}_3)_3$, and $\text{Si}(\text{CH}_3)_3$] promises to be interesting.

The kinetics of the thermal decomposition of the $(\text{CH}_3)_nAlNH_n$ ($n = 3, 2$) compounds has been studied in detail using NMR and DSC measurements with the help of a visiting professor from King's College during two summers and a sabbatical year in our laboratory. This latter study is the subject of a paper (paper 5 in Appendix I) which will shortly be submitted for publication to J. Am. Chem. Soc. As a result of the kinetic study, a mechanism involving the autocatalytic elimination of methane from the $(\text{CH}_3)_nAlNH_n$ ($n = 3, 2$) compounds was postulated which accounts for facile

conversion of these precursors to RAlNH and subsequently AlN . A role for ammonia in the alignment and fusion of six-membered Al-N rings during these transformations is also suggested.

Our studies of SiC precursors have centered on the synthesis of polycarbosilanes by the Grignard reaction of $\text{ClRR}'\text{SiCH}_2\text{Cl}$ compounds. We have carried out this reaction with $\text{R},\text{R}' = \text{Cl}$ and $\text{R} = \text{Cl}$ and $\text{R}' = \text{CH}_3$, as well as $\text{R},\text{R}' = \text{phenyl}$, and obtained both polymeric and oligimeric products of the type $[\text{RR}'\text{SiCH}_2]_n$. Subsequent reduction of the Cl-containing products with LiAlH_4 has yielded the corresponding Si-H materials. The $\text{R} = \text{CH}_3$, $\text{R}' = \text{H}$ derivative was used in the co-pyrolysis experiments with the alkyaluminum amides (vide infra). In the absence of the AlN precursor, this system gives very low ceramic yields of SiC (ca. 20%); however, in the presence of 5-25 mole% (*i*-butyl) AlNH_2 , the ceramic yield is enhanced by as much as 2X. The origin of this effect is still under investigation; however, it is clear that a variety of novel chemical interactions involving the organoaluminum and organosilicon species are occurring in this precursor mixture during co-pyrolysis.

The fully H-substituted system, $[\text{SiH}_{2-x}\text{CH}_2]_n$, has a high ceramic yield (up to 97% on slow heating) and undergoes hydrosilation reactions with divinyl silanes to yield gels and glassy solids. The study of these systems as a source of SiC is continuing, with emphasis on understanding of the structures, physical properties, and the thermal and chemical reactions of the various polycarbosilane derivatives. Similarly, work on the novel organoaluminum precursors developed in the course of this research program and their interaction with the organosilicon compounds is also continuing. Future publications describing the results of these ongoing investigations which have been spawned by our AFOSR-sponsored research are anticipated over the next few years.

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- 3 L.V. Interrante, W. Lee, M. McConnell, N. Lewis and E. Hall, *J. Electrochem. Soc.*, in press.
4. C.J. Schilling, Jr. J.P. Wesson, T.C. Williams, *Ceram. Bull.* **62**, 912 (1983).
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6. XRD data on this product indicates that the major crystalline phase is a β' -SiAlON: $a = 7.647$, $c = 2.938$, with a minor component of α -Si₃N₄; $a = 7.77$, $c = 5.66$ (Figure 2). Based on the lattice parameters an approximate 'z' value for the composition Si_{6-z}Al_zO_zN_{8-z} has been estimated to be between 1.3 and 2.2 [L. Gillott, et. al. *J. Mater. Sci.* **16**, 2263 (1981)]. The theoretical 'z' value for the expected 1:3 Al:Si composition of this sample is 1.55.
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APPENDIX I

PAPERS RESULTING FROM THE AFOSR CONTRACT RESEARCH

1. M.L. Hackney, L.V. Interrante, G.A. Slack, P.J. Schields, "Organometallic precursors to $\text{Si}_{\frac{w}{x}}\text{Al}_{\frac{y}{x}}\text{C}_{\frac{z}{x}}\text{N}_{\frac{z}{x}}$ Ceramics," Proc. 3rd International Conference on Ultrastructure Processing of Ceramics, Glasses, and Composites, J.D. McKenzie and D.R. Ulrich, eds., J. Wiley, Publ., (1988), p.99.
2. L.V. Interrante, C.L. Czekaj, M.L.J. Hackney, G.A. Sigel, P.J. Schields, and G.A. Slack, "An Investigation Into the Preparation, Properties, and Processing of SiC/AlN and Si_3N_4 /AlN Ceramics from Organometallic Precursors," MRS Sympos. Proc. 121, 465 (1988).
3. C.L. Czekaj, M.L.J. Hackney, L.V. Interrante, G.A. Sigel, P.J. Schields, G.A. Slack, "Preparation of SiC/AlN and Si_3N_4 Ceramics Using Organometallic Precursors," submitted for publication to *J. Amer. Cer. Soc.*
4. L.V. Interrante, G.A. Sigel, C. Henja, and M. Garbauskas, "Organometallic Precursors to AlN: Synthesis and Crystal Structures of $[\text{Me}_2\text{AlNH}_2]_3$ and the Planar Species $[(\text{t}-\text{butyl})_2\text{AlNH}_2]_3$ ", *Inorg. Chem.* 28, 252 (1989).
5. L.V. Interrante, G.A. Sigel, C. Henja, and M. Garbauskas, "Cyclic $(\text{AlN})_n$ Compounds as Precursors to AlN: Synthesis and Structures of $[\text{Me}_2\text{AlNH}_2]_3$ and the Planar Species $[(\text{t}-\text{butyl})_2\text{AlNH}_2]_3$ ", *Phosphorous, Sulfur and Related Elements*, in press.
6. F. Sauls, L.V. Interrante, C.L. Czekaj and Z. Jiang, "Me₃AlNH₃ Formation and Pyrolytic Methane Loss; Thermodynamics, Kinetics and Mechanism", to be submitted to *J. Amer. Chem. Soc.*

5

COMPLETED PROJECT SUMMARY

1. TITLE: PREPARATION OF SiC/AlN SOLID SOLUTIONS USING ORGANOMETALLIC PRECURSORS

2. PRINCIPAL INVESTIGATOR: L.V. INTERRANTE

3. INCLUSIVE DATES: September 30, 1985 - December 31, 1988

4. CONTRACT/GRANT NUMBER: F49620-85-0019

5. COSTS AND FY SOURCE: total cost: \$339,185; \$116,060 FY 88

6. SENIOR RESEARCH PERSONNEL: Dr. M. Hackney Dr. C Czekaj
Dr. G. Sigel Dr. F. Sauls

7. JUNIOR RESEARCH PERSONNEL: Mr. C. Whitmarsh
Mr. Z. Jiang
Mr. H-J. Wu
Ms. P. Brown

8. PUBLICATIONS:

1. M.L. Hackney, L.V. Interrante, G.A. Slack, P.J. Schields, "Organometallic precursors to $\text{Si}_{\text{w}}\text{Al}_{\text{x}}\text{C}_{\text{y}}\text{N}_{\text{z}}$ Ceramics," Proc. 3rd International Conference on Ultrastructure Processing of Ceramics, Glasses, and Composites, J.D. McKenzie and D.R. Ulrich, eds., J. Wiley, Publ., (1988), p.99.
2. L.V. Interrante, C.L. Czekaj, M.L.J. Hackney, G.A. Sigel, P.J. Schields, and G.A. Slack, "An Investigation Into the Preparation, Properties, and Processing of SiC/AlN and Si_3N_4 /AlN Ceramics from Organometallic Precursors," MRS Sympos. Proc. 121, 465 (1988).
3. C.L. Czekaj, M.L.J. Hackney, L.V. Interrante, G.A. Sigel, P.J. Schields, G.A. Slack, "Preparation of SiC/AlN and Si_3N_4 Ceramics Using Organometallic Precursors," submitted for publication to *J. Amer. Cer. Soc.*
4. L.V. Interrante, G.A. Sigel, C. Henja, and M. Garbauskas, "Organometallic Precursors to AlN: Synthesis and Crystal Structures of $[\text{Me}_2\text{AlNH}_2]_3$ and the Planar Species $[(\text{tert-butyl})_2\text{AlNH}_2]_3$," *Inorg. Chem.* 28, 252 (1989).
5. L.V. Interrante, G.A. Sigel, C. Henja, and M. Garbauskas, "Cyclic $(\text{AlN})_n$ Compounds as Precursors to AlN: Synthesis and Structures of $[\text{Me}_2\text{AlNH}_2]_3$ and the Planar Species $[(\text{tert-butyl})_2\text{AlNH}_2]_3$," *Phosphorous, Sulfur and Related Elements*, in press.
6. F. Sauls, L.V. Interrante, C.L. Czekaj and Z. Jiang, "Me₃AlNH₃ Formation and Pyrolytic Methane Loss: Thermodynamics, Kinetics and Mechanism", to be submitted to *J. Amer. Chem. Soc.*

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COMPLETED PROJECT SUMMARY

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9. ABSTRACT OF OBJECTIVES AND ACCOMPLISHMENTS:

The co-pyrolysis of organoaluminum and organosilicon compounds was investigated as a potential source of SiC/AlN solid solutions. Using two different co-pyrolysis methods, homogeneous mixtures of organoaluminum amides and both a vinylic polysilane and a polycarbosilane were converted to a preceramic solid that transformed to crystalline SiC/AlN solid solutions at <1600 °C. Moreover, the liquid, polymeric, form of these precursor mixtures provides a potential processing advantage that may be useful for ceramic matrix preparation and other applications. In the course of this work new precursors to both AlN and SiC were identified and their structures and pyrolysis reactions were investigated, providing useful information regarding structure/pyrolysis chemistry relationships for such precursor systems.

In addition, modifications of this co-pyrolysis approach to SiC/AlN solid solutions were employed to obtain mixed-phase SiC/AlN, silicon nitride, silicon nitride/AlN and β' -SiAlON ceramics. The composition, phase distribution, and microstructure of these ceramics were examined by elemental analysis, x-ray powder diffraction, SEM/TEM, and other methods. This effort was successful not only in yielding processible precursors to the desired SiC/AlN solid solutions, but also in providing a general route to a wide range of other compositions and phases in the Si-C-Al-O-N system.